

DISTRIBUTION OF IMPREGNATED METAL HALIDE CATALYSTS IN COAL GRAINS

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INTRODUCTION

Metal halides such as stannous chloride and zinc chloride are known to be effective coal hydrogenolysis catalysts (1-3). Weller et al. (1) examined a number of potential catalysts and found zinc and tin chlorides to be among the best. Although stannous chloride is generally recognized to be more active than zinc chloride, zinc chloride has been chosen as the catalyst in a number of coal liquefaction systems. These include processes developed in Japan (4), molten salt reactors (2,3) and short residence time reactors (5-7).

The metal halides appear to be active in cleaving bridges between groups of condensed aromatic rings (unit structures) under liquefaction conditions. This results in a progressive depolymerization of the coal, ultimately to isolated unit structures, with little reaction of the condensed ring systems themselves (8-10). This results in less hydrogen consumption and a soluble product that can be further upgraded. Weller et al. (1) suggested that a metal sulfide was formed, which was the active catalytic species. Zielke et al. (2) proposed a complex of zinc chloride and water to form a Friedel-Crafts type acid, for the case of zinc chloride catalyzed liquefaction. Bell and coworkers (11-14) studied the cleavage in model compounds with ether and carbon-carbon bonds, species that are thought to form bridges between unit structures in coal. They proposed a similar active species. This conclusion was supported by a study of Beishline et al. (15). The hydrogenolysis reaction begins at the surface of coal grains and proceeds towards the center (16,17). As the bridges are broken, the coal softens and reacts. The metal halides lower the temperature at which the coal softens (18) and also the temperature at which the exothermic coal hydrogenation reaction occurs (19).

Contacting of the metal halide with the bridging structures is required for the liquefaction reaction to proceed. At the temperatures of liquefaction processes, the coal softens and both thermal and catalytic bond cleavage occurs. The reactions are rapid, but may lead to retrogressive reactions if sources of hydrogen are insufficient or the catalyst is not present (20,21). The semi-coke formed by the retrogressive reactions is less reactive to liquefaction and increases the reaction time and severity of conditions required for high conversions. Partial liquefaction under hydrogen deficient conditions may induce sufficient fluidity for mesophase to form. Recently, the liquefaction of coal at mild conditions, below the normal softening temperature, has been studied (22). The process involves two steps: hydrotreating of metal halide impregnated coal and base catalyzed depolymerization of the products. The temperature of the process is kept below 275°C. Under these conditions, the fluidity of the system is low and it is important to have good contact between the metal halide catalyst and the bridges that are to be cleaved. The catalytic reactions must occur and the thermal reactions must be suppressed. It is therefore important that a good dispersion of the catalyst throughout the coal grains be achieved. The effect of impregnation method on the dispersion of the catalyst is the subject of this report.

EXPERIMENTAL

Four coal samples were studied in these experiments. The ultimate analysis of the coals is shown in table 1. The preparation of the samples for analysis is shown schematically in figure 1. The coals were ground to -60/+100 mesh and extracted with THF in a Soxhlet extractor. Some samples used for X-ray analysis were demineralized by HCl and HF. Water, acetone and methanol were used as solvents for impregnation of the metal halides. Reagent grade ZnCl_2 , FeCl_3 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were impregnated on the coals. The solvent, metal halide and coal were mixed in the desired amounts. The mixture was stirred and agitated in an ultrasonic bath for two hours. The coal/metal halide mixture was then dried to remove the solvent.

Grain mounts were prepared with epoxy mounting medium, ground and polished to expose cross sections of the coal grains. A Hitachi (model S-500) scanning electron microscope was used to examine the samples. The electron energy was 20,000 KeV. A Kevex energy-dispersive spectrometer was used to map fluorescent X-rays from the metal atoms and the chlorine. X-ray diffraction was used to measure changes in the spacing of clusters of condensed-ring aromatic groups. The assignment of X-ray diffraction peaks was by comparison with the diffraction pattern of graphite.

RESULTS AND DISCUSSION

Polished grain mounts of the metal halide-impregnated coal samples were examined with the scanning electron microscope. Grinding and polishing of the grain mounts exposes a cross section of the coal grains. Fluorescent X-rays, emitted from the surface of the mount, were measured with the energy dispersive detector as the sample was scanned. A narrow band of X-rays, corresponding to a specific atom, were recorded on photographic film as the sample was scanned. The distribution of the given atom in the coal grain was thus obtained. The metal atom and chlorine atom distributions for various impregnation conditions were determined. If the metal halide is uniformly distributed throughout the coal grain, the photograph will show a uniform exposure throughout the cross section of the coal grain. If the metal halide is poorly distributed throughout the coal grain, the photograph will show exposure at the edge of the cross section and along cracks, but not in the center of the grains. Some background exposure will be seen in areas where the epoxy mounting medium is exposed at the surface. Electron micrographs of the coal grains were also obtained. The X-rays mostly originate near the surface, since the depth of penetration of the electrons is not great.

The distribution of the metal halides within coal grains is qualitatively shown in figure 2. The interpretation is subjective and is based on observation of several grains for each sample. Good dispersion of the metal halides is achieved with organic solvents. Both methanol and acetone are effective in dispersing the metal halides and under the conditions of these experiments, it is impossible to determine if one is better than the other. Both of these solvents are known to swell coals. Stannous chloride is the most easily dispersed of the metal halides tested. Nickel and iron chlorides are more difficult to disperse from aqueous solution. The effectiveness of dispersion of the metal halides varies with the coal samples, but does not follow rank.

Beall (23,24) has reported the possible formation of intercalation compounds of coal with the chlorides of iron, chromium, and copper at temperatures from 215°C to 150°C. The formation of intercalates has been suggested as a possible mechanism in the catalysis of coal hydrogenolysis by metal halides. The possible formation of intercalates was investigated by X-ray diffraction of the impregnated samples. Formation of an intercalation complex would be expected to shift the 002 diffraction peak, corresponding to a larger interplanar spacing in the clusters of condensed-ring aromatic groups. Demineralized samples were studied to remove the interference from diffraction peaks due to mineral matter. Impregnation of metal halides decreased the intensity of 002 diffraction peaks due to scattering of X-rays by the metal atoms, but the peaks were not shifted. Although the formation of intercalates cannot be ruled out by these experiments, there is no evidence to support intercalate formation.

Acetone and methanol swell coals and are also effective in impregnating metal halides throughout the coal structure. Examination of swollen coals, from which the solvent has been removed, by X-ray diffraction show no changes in the 002 diffraction peak. The solvent is apparently imbibed by the amorphous regions surrounding the clusters of condensed-ring aromatic units, but does not disrupt the clusters. The metal halides appear to be deposited in these amorphous regions as the solvent is evaporated. Water does not swell coal, but it is adsorbed on coal surfaces within pores. Impregnation from aqueous solution is not as effective as from organic solution and depends strongly on the coal and the metal halide properties. Impregnation of stannous chloride from aqueous solution at room temperature can be quite effective in achieving high dispersion at the microscopic level, which is the limit of resolution of these techniques. The dispersion at the molecular level for impregnation from either aqueous or organic solutions cannot be measured by these procedures.

CONCLUSIONS

Impregnation of metal halides throughout coal structures is more effective from organic solutions than from aqueous solutions. High dispersion of the metal halide is attributed to the ability of the solvent to penetrate the coal structure and cause swelling. A minimum solubility of the metal halide in the solvent is also required. No evidence for the formation of intercalation compounds between the metal halides and condensed-ring aromatic structures in the coal has been found.

Good dispersion of potential coal hydrogenolysis catalysts throughout the coal is expected to be important in low-severity coal liquefaction processes. Liquefaction may be expected to be achieved below the normal softening temperature of the coal. Good dispersion may also prevent the formation of less-reactive semicoke during liquefaction at higher temperatures. Under conditions of good catalyst dispersion and hydrogen accessibility, depolymerization of coal to soluble products may be expected to occur rapidly.

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Table 1. Ultimate Analysis of Coal Samples

	Wyodak	Burning Star	Elkhorn	Coal Basin
Carbon, %	76.0	78.9	85.4	90.3
Hydrogen, %	5.4	5.4	5.1	5.4
Nitrogen, %	1.4	1.2	1.8	2.2
Sulfur, %	0.6	4.4	0.7	0.7
Oxygen, % (dif)	16.6	10.1	7.0	1.4

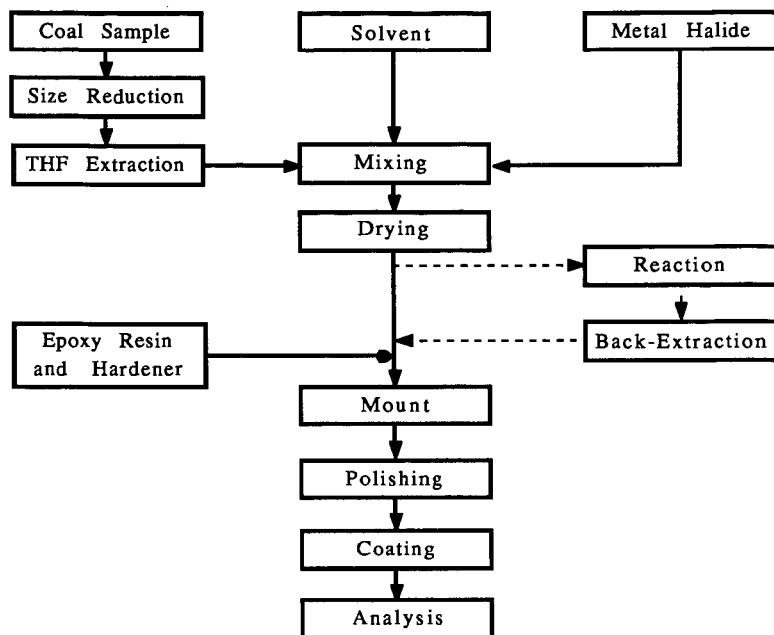


Figure 1. Flowchart for SEM Mount Preparation

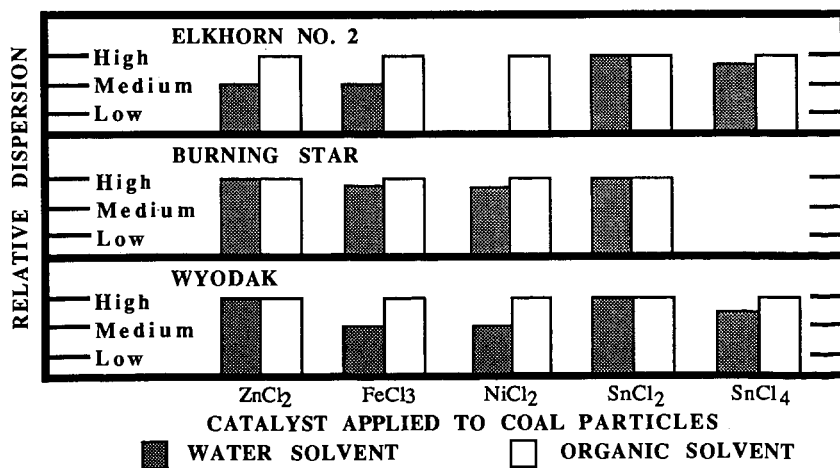


Figure 2. Catalyst Dispersion